Faculty of Manufacturing Engineering

MICROSTRUCTURAL CHARACTERIZATION AND FRACTURE OBSERVATION OF GREEN INNOVATIVE GLASS (GIG) CERAMIC TILES PRODUCED BY SINTER CRYSTALLIZATION OF WASTE GLASS

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A thesis submitted in fulfilment of the requirements for the degree of Master of Manufacturing Engineering (Advanced Materials and Processing)

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DECLARATION

I declare that this thesis entitled "microstructural characterization and fracture behaviour of green innovative glass (GIG) ceramic tiles produced by sinter crystallization of waste glass" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree

Signature:

Name: Aina Syuhada' binti Ahmad

Date:

APPROVAL

I hereby declare that I have read this thesis and in my opinion this thesis is sufficient in terms of scope and quality for the award of Master of Manufacturing Engineering (Advanced Materials and Processing)

Signature:

Supervisor Name: Associate Professor Dr. Jariah binti Mohamad Juoi

Date:

DEDICATION

Especially dedicated to my beloved parents, family, lectures, and all individuals for their motivation, love and attention has made it possible for me to reach up to this point and also for my supervisors who be the best mentor and supervisors and always showing me guidance for my project.

ABSTRAK

"Jubin Seramik Kaca Inovatif Hijau (GIG)'' adalah jubin seramik yang menggunakan serbuk sisa kaca daripada sisa perbandaran. Bahan mentah asas yang digunakan untuk fabrikasi GIG adalah sisa kaca silika kapur soda (SLSG) yang dikumpulkan dari PUM Cullet SDN BHD. terletak di Johor Bharu. Didapati bahawa jubin GIG mempunyai kekuatan mekanikal yang lebih tinggi berbanding dengan jubin seramik konvensional yang ada di pasaran. Perlu diingatkan, bahawa jubin seramik GIG dihasilkan melalui mekanisme pensinteran likat pada suhu pensinteran 850^{o}C dan tenaga yang lebih rendah berbanding dengan jubin seramik konvensional. Sebaliknya, jubin seramik konvensional dihasilkan melalui mekanisme pensinteran keadaan pepejal pada suhu yang lebih tinggi iaitu 1200^{o}C. Sehubungan itu, objektif projek ini adalah untuk mencirikan GIG menggunakan XRD dan SEM, untuk membandingkan mikrostruktur dan tingkah laku patah jubin GIG dan jubin porselin seramik konvensional (tidak berlicau) dan untuk menjelaskan hubungan komposisi proses dan sifat mekanikal dengan mekanisme pensinteran jubin GIG dan jubin porselin seramik konvensional (tidak berlicau). Analisis mikrostruktur menggunakan imageJ, SEM, dan XRD dilakukan terhadap kelakuan patah jubin GIG dan jubin porselin seramik konvensional (tidak berlicau). Seterusnya, perbandingan prestasi mekanikal dan tingkah laku patah yang berkaitan dengan fasa hablur dan mikrostruktur GIG dan jubin porselin seramik konvensional (tidak berlicau) dilakukan melalui analisis dapatan dan kajian persuratan. Analisis keliangan menggunakan imageJ menunjukkan porselin seramik konvensional (tidak berlicau) mengandungi 0.25%, jubin GIG hijau mengandungi 0.80% dan GIG putih mengandugi 0.97% keliangan. Analisis XRD menunjukkan bahawa jubin porselin seramik konvensional (tidak berlicau) terdiri daripada fasa kuartza sementara GIG putih dan hijau mengandungi wollastonit, kristobalit, dan fosterit. Analisis SEM menunjukkan ciri retak menjajar berpunca daripada kehadiran butiran besar pada jubin porselin seramik konvensional (tidak berlicau). Manakala, sampel GIG menunjukkan kelakuan patah dengan ciri mikroretak yang lebih tersebar kesan patah transgranular dan intergranular. GIG hijau menunjukkan retakan yang paling dalam berikutan dapat menyingkirkan tekanan dengan hanya sedikit pemanjangan.

ABSTRACT

Green Innovative Glass (GIG) Ceramic tile is a ceramic tile that uses waste glass powder arising from municipal wastes. The basic raw material used for fabricating GIG is soda lime silica glass (SLSG) waste which was collected from PUM Cullet SDN BHD. located in Johor Bharu. Most of this cullet were originated from waste glass containers or bottles. It was found that the quality of GIG tiles is of increased mechanical strength compared to the conventional tile in the market. It should be noted that the GIG tile is produced by viscous sintering at lower sintering temperature of 850^{o}C and lower energy than the conventional tile which is produced by solid-state sintering mechanism at higher sintering temperature of commonly 1200^{o}C. Thus, the objective of this work is to characterize the green innovative ceramic (GIG) tile using XRD and SEM, to compare the microstructural properties and fracture behaviour of GIG tiles and unglazed porcelain conventional ceramic tiles and to explain the relation of composition with process and mechanical properties related to the sintering mechanism of GIG tile compared to unglazed porcelain conventional ceramic tile. The microstructural analysis of GIG tile using imageJ, SEM, and XRD is carried out with attention given to its mechanical performance and fracture behaviour. Then, a comparison on the mechanical performance and fracture behaviour related to the crystal phases and microstructural present of GIG and unglazed porcelain conventional ceramic tile is carried out using reported findings via comprehensive literature review. It was found by the imageJ analysis that 0.25%, 0.80% and 0.97% porosity exist in the unglazed porcelain conventional ceramic tile, green GIG and white GIG respectively. The XRD analysis shows that unglazed porcelain conventional ceramic tile consists of Quartz phase while the white and green GIG consists of wollastonite, cristobalite, and fosterite. SEM analysis shows that the fracture behaviour of the unglazed porcelain conventional ceramic tile is having an alignment of crack propagation originated to large grains in the material. While, in the GIG samples cracks propagate more disperse and caused by the microcracks due to transgranular and intergranular fracture. Green GIG shows the deepest crack as it is able to repel lots of stress with less elongation.

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CHAPTER 1

INTRODUCTION

1.1 Background

Ceramic tile is a product that attracted attention from the designer and manufacturers for its low water absorption and high mechanical strength. The properties of the ceramic tile due to its low porosity which is caused by the processing conditions such as having high degree milling of raw materials, high sintering temperature, high force compaction and high desiccation. Moreover, ceramic tile is widely used for the past years because they have a wide range of properties and certain tiles are better suited for some installations than others. Few tiles are suited for all types of installations and precise knowledge of the tile properties is necessary for the consumer to achieve the desired and expected value of the tile. The ceramic tile sold in the market must pass quality assurance test such as MS ISO sirim standard, ASTM tests and the values of each performance test are crucial for manufacturers, designers, and sellers.

The ceramic industries are based mostly on the production of clayey ceramic materials for use as roofing tiles and wall tiles (Santos, 1989). The raw material used for the manufacture of ceramics is basically the common clays. The major composition of clay is silica, SiO_2 and alumina, Al_2O_3 utilised in the production of ceramic product with adding up with other materials to obtain the desired standard. Nowadays, ceramic tile made from glass waste have been studied to recycle or reused the waste which were being deposited in landfills for economic purpose and more sustainable environment (A. S. Ogunro *et al.*, 2016). The conversions of waste to wealth have lead to zero waste.

The conventional ceramic tile and the glass ceramic tile undergo different sintering processes which are via solid state sintering and viscous sintering, accordingly. Sintering process is the most crucial stages in the fabricating of the tiles. The changes of microstructure happen along this process will making the essential final properties for example, mechanical strength, and protection from chemical agents size steadiness and easy cleaning. The major factors in the thermal cycle amid the sintering stage are the firing time and temperature and the furnace air which depend on the composition of the raw materials and the kind of product required. Sangsom Chitwaree et al. (2018) found that conventional ceramic tiles, C sample which represented for the porcelain tiles made up of 5% wt ball clay, 10wt% kaolin clay and 40wt% kaolin clay sintered at high temperature of 1230^{o}C have higher material cost and energy cost compared to the glass ceramic tile, N sample made up of 50% pottery stone and 50% recycled glass as shown in Table 1.1. Moreover, the energy consumption in the sintering process could reduce about 30% when compared with that of the conventional ceramic tiles and based on these results, recycled soda- lime glass was commence to promote viscous flow which occurred at lower sintering temperature of 1050^{o}C. Furthermore, it is believed that sintering mechanism such as the solid state sintering and influences the microstructural properties of the ceramic tile and the glass ceramic tile.

Table 1.1 Material and Process Costs of The N Sample and The C Sample (Sangsom Chitwaree et al, 2018)

Production cost	N sample ($/kgProduct) 1050 °C	C sample ($/kgProduct) 1230 °C
Raw material cost	0.29	0.42
Energy cost[a] (sintering process)	0.13	0.19

1.2 Problem Statement

In previous work (Wani, 2016), new green Ceramic tile made from waste term as Green Innovative Glass (GIG) ceramic tile is produced from waste glass and industrial waste which varied from the conventional ceramic tile on the market. The waste materials involve are soda lime silicate glass which is the waste glass arising from domestic use such as bottles and container, spent bleach earth from oil palm refineries industries and incinerated ash of oil sludge from petrochemical industries. The production of this product would add value to the waste produced in the society. It saves natural raw materials and recycling waste into marketable product. Moreover, it reduce land requirement for waste disposal and innovate new practice of waste glass recycling.

The Soda lime silicate glass is the most familiar type of glass used which is made up of about 75% silica, SiO_2 addition of about 15% sodium oxide,Na_2O, 12% calcium oxide, CaO (Erhan K., 2015). Glass plays a vital role in science and technology. They are suitable for various applications, such as, flat glass, container glass, optoelectronics and optics material, laboratory equipment, thermal insulator, reinforcement concrete, glass art due to the chemical, physical and optical properties of the glass. Glass also can resist chemical interactions, does not leach chemicals like plastics and it can withstand heat and cold.

According to Wani (2016), both green and white GIG ceramic tile have lower porosity percentage with increasing bulk density and lower corrosion rates. Throughout the study, sintering temperature, particle size, pressure used and glass content influenced the properties of the glass composites.

Ashraf M. (2019) claimed that the green GIG ceramic tile possess highest stress with lowest stroke or displacement in the length during flexural testing. It was also reported that Green and White GIG ceramic tile consist of mainly wollastonite, cristobalite, and fosterite as shown in Figure 1.1. This whole phase consists of mainly silicon oxide, calcium oxide and magnesium oxide. In GIG ceramic tile, an additional powdered glass in the composition of which came from the wasted drinking glass bottle meanwhile, there was no present of waste glass in the conventional ceramic tile. Increases of the Silicon element into the ceramic tiles due to the glass bottles are made up of soda-lime silicate. The glass powder acts as a binder between the grain of the clay ball and melt into a glassy phase which holds the grain tighter and thus results in such high mechanical properties (Mustaffar et al., 2017).

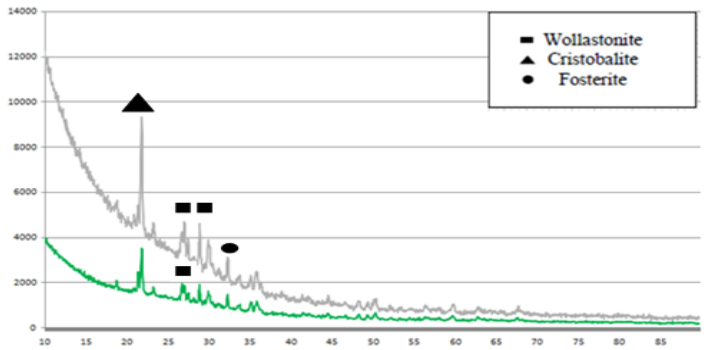

Figure 1.1 Phases Analysis For White GIG (white line) and Green GIG Ceramic Tile (green tile)

Quality of the GIG ceramic tile is of increased mechanical strength compared to those in the market and produced at lower cost. This is due to the sinter crystallization via viscous flow sintering at lower temperature during the processing. To understand the sintering mechanism and microstructural evolution taking place during sintering, details microstructural characterization is carried out. The microstructural characterization had enabled to scientifically explained the increased mechanical strength observed relating to the sintering. Moreover, in depth analysis on the fracture behaviour of GIG ceramic tile samples upon subjected to mechanical loading during the flexural test also enable to relate the performance of the GIG ceramic tile with its microstructure features. This observation was compared with the fracture behaviour of conventional ceramic tile. This had enabled better understanding of the materials-processing and performance of GIG ceramic tile related to its sintering mechanism.

1.3 Objective

The current study mainly focus on study of microstructural characterization of GIG ceramic tiles produced by viscous sintering and conventional tiles produced by solid state sintering mechanism. The objectives of this study are:

1) To characterize the green innovative glass (GIG) ceramic tile using XRD and SEM.
2) To differentiate the microstructural properties and fracture behaviour of GIG ceramic tiles with the unglazed porcelain conventional ceramic tiles.
3) To explain the relation of composition with process and mechanical properties related to the sintering mechanism of GIG ceramic tile compared to unglazed porcelain conventional ceramic tile.

1.4 Scope

The scopes of this study are:

a) Characterization of the GIG ceramic tile with ratio of Soda Lime Silica Glass, SLSG to ball clay of 90:10 weight percent,wt.% by using XRD and SEM
b) Characterization of the GIG ceramic tile with ratio of SLSG to ball clay of 85:15 wt% by using XRD and SEM

c) The GIG ceramic tile with ratio of SLSG to ball clay of 90:10 wt% is labelled as the white GIG ceramic tile, while the GIG ceramic tile with ratio of SLSG to ball clay of 85:15% wt% is labelled as the green GIG ceramic tile.
d) External data research about the microstructural properties, composition, process, sintering mechanism and mechanical properties of the conventional ceramic tile and the GIG ceramic tile gained from literature review for comparison and broaden the knowledge about the unglazed porcelain conventional ceramic tile and GIG ceramic tile from various researchers.
e) Analysis of microstructural properties of GIG ceramic tile produced by viscous sintering using imageJ, XRD and SEM.
f) Analysis of microstructural properties of unglazed porcelain conventional ceramic tile produced by solid-state based on the literature review.
g) Broaden knowledge about conventional ceramic tile gain from literature review but unglazed porcelain conventional ceramic tile is chosen for comparison with GIG ceramic tiles on the analysis of microstructural properties and fracture observation.

CHAPTER 2

LITERATURE REVIEW

2.1 Conventional Ceramic Tiles: Composition and Processing

Generally, there were 3 types of conventional ceramic tile which are the ceramic mosaic tiles, the glazed floor tile and porcelain tile. The ceramic mosaic tile is commonly fired to water absorptions of less or equal to 0.1% and feldspar was used for a flux, and ball clay or kaolin used for the clay fraction in the ceramic tile body. Meanwhile, the glazed floor tile usually fired to 2% to 3% water absorption. Feldspar or a local flux and ball clay are required for the plastic fraction of the tile composition. The appearance or color of the tile body is not an issue because this tile has a 100% glazed surface. The porcelain tile is a high temperature floor tile which fired to less or equal than 0.1% water absorption. It is used in mainly the demanding commercial applications due to their high strength. Only a portion of the tile surface is decorated thus, the appearance or body color is crucial. The tile required feldspar or nepheline syenite as a flux. Ball clay and kaolin usually used in the plastic fraction in the body (Grahl C., 2002)

Table 2.1 displays the raw materials in percentage consumed by tile production in Mexico (Jose M. *et al.*, 2014). It can be seen that the producers of ball clay gained profit from the higher percentage of ball clay contain in the ceramic tile. The consistent processing and chemical characteristics of commercially produced ball clay were essential for porcelain tile, however the engineered clay blends designed to meet specific customer formulations must be used. Therefore, the technical potential and support available from the clay producer has become increasingly critical to maintain customer relationships.

Table 2.1 Raw Materials In Percentage For Each Tile Product (Jose M., 2014)

Product	Ball Clay, %	Calcium carbonate, %	Kaolin, %	Silica, %	Feldspar, %	Talc, %	Wollas tonite, %	Shale Flux
Ceramic Tile	452	40	160	217	398	14	9	
Porcelain Tile	23		19	5	52	1		
Glazed Tile	45							55

The starting point for the manufacturing process is a series of raw materials which go through transformation in order to attain the desired properties of the finished product. Product quality is related to the composition of raw materials utilised and the procedure took place during manufacturing.

Figure 2.1 shows the processing flow diagram to form a ceramic product which using uniaxial dry pressing. The batch consists of granular and powder materials that on firing consolidate and shrink into a denser mass. The powder for ceramic tile is dispersed clay and ground materials. Water acts as solvent for reason of safety, cost and availability. The batches contain moisture range from 4 to 8wt% although it is called dry pressing method. Pressing additives is needed to assist in developing the required pressed density and microstructure with a minimum of variability over the piece and within a production of tile. The pressing additives could be organic or inorganic in nature and might be utilised in combination. Batch’s mixing is a very crucial phase as it strongly influences the homogeneity of the product. Dispersion of agglomerated batch ingredients is also vital component of the mixing operation.

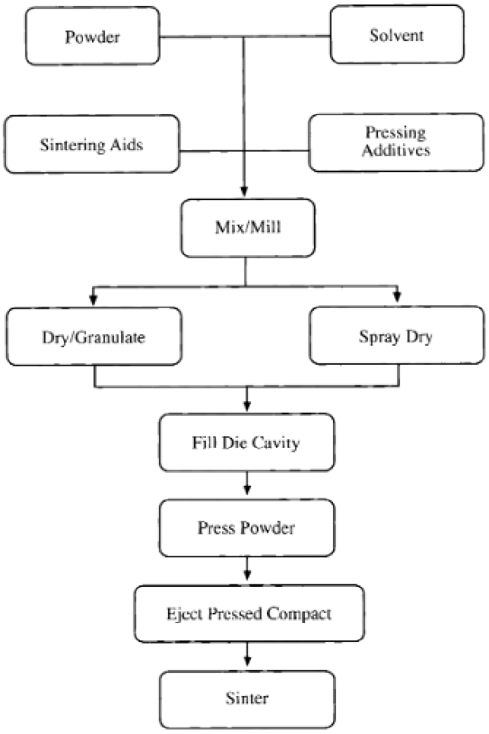

Figure 2.1 Flow Diagram For The Process To Form Ceramic Product (James S.Reed, 2000)

Milling might be combined with mixing in one operation that is used to reduce the sizes of larger primary particles and aggregates, to decrease the average particle size of the batch and to chemically change surfaces of particles on a microscopic level. Rapid dry pressing needed a granulated free flowing material. Granulation is achieved using either a dry processor in a wet process that is commonly spray drying. A granule is the controlled agglomerates produced in the process. Granules are mechanically pressed via uniaxial dry pressing to form the unfired tile.

Granules must deform in a controlled manner enabling the formation of a denser, shaped product with adequate strength for following handling including any surface finishing operations throughout the pressing operation. The batch of materials must able to being processed efficiently into a feed material that can be easily pressed and then sintered via solid-state sintering mechanism at sintering temperature of more than 1150^{o}C to produce a tile product with controlled strength, density and surface characteristics.

2.2 GIG Ceramic Tiles: Composition and Processing

The basic raw material utilised in this project is soda lime glass waste, SLG which is collected from PUM Cullet Sdn. Bhd located at Johor Bharu. The glasses were collected from waste glass container or bottles. The compositions of each of the GIG ceramic tile are shown in Table 2.2.

Table 2.2 Composition Of GIG Ceramic Tile (Wani, 2016)

GIG ceramic tile	Soda Lime Silicate Glass, SLSG	Clay	Moisture
White GIG ceramic tile	90%	10%	8%
Green GIG ceramic tile	85%	15%	8%

According to Wani (2016), the process to form GIG ceramic tile is shown in Figure 2.2. Firstly, GIG ceramic tiles fabrication started with the formulation preparation including the raw material preparation and the treatment of material as it follows the research constraint characteristics. The sizing of raw material, SLG is processed by crushing using the jaw crasher and milling using ball mill. The ratio of grinding media is 1: 2. 2 portions of material are added by one portion of medium. The purpose of grinding media is to break the material size during the process. The powder were produced by the end of this process before undergo the following step.

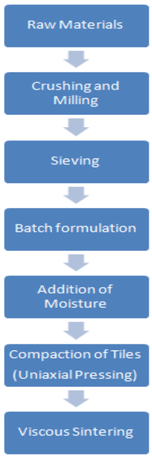

Figure 2.2 Flow Diagrams for the Process to Form the GIG Ceramic Tile

Next, crushing and milling process took place at room temperature for 24 hour and the speed is depend on the ball mill machine. The grinding media is alumina and cannot be steel/SS media because the powder can be contaminated during grinding process due to high ferum component in the media. The effect of using steel/SS media is shown by the changes of powder colour from white to gray (Non-coloured SLG).

Then, sieving step was carried out. The sieving is carried out to make sure the homogeneous size of formulation is formed. The moisture will be sprayed to the powder material according to its percentage out of the total weight of the powder. The common moisture content using in the ceramic industry is from 5-10%. One of common phenomenon occurred is the material will not pass through the test sieve due to the wet material condition. Some researchers tend to sieve the material manually using paint brusher in order to make it easier rather than grinding it again. Unfortunately, it'll make the material size become non-homogeneous.

Drying the material in oven about 4-5 hours is one of method to sieve the material properly. The temperature of the oven can be estimate around 120 until 150 celcius. Eventually the material will become dry and it will pass through the test sieve easily. Also the drying will not change the chemical composition of the powder materials.

After that, the powder material will undergo the process of batch formulation. In this process, the raw material and the binder will be mixed together. The binder/filler is used in sintering process of the ceramic tiles later. The duration time of mixing is one hour by using the ball mill machine and HDPE bottle. One of precaution step is changing the bottle after 18 hours used in order to avoid the contamination of the material.

Next is the moisture addition. The addition of the moisture is a need in the compaction or pressing process of the ceramic tiles. The vital item to make sure the tiles are binding properly is moisture content. The moisture will be added to the formulation by spraying manually the moisture 6% from actual weight. Then, the formulation will be put in the dessicator about 2 hours before it will be sieved by test sieve 600-800mm(the size of the test sieve is not important as long as the material can pass through the test sieve properly).

Uniaxial pressing as shown in the Figure 2.3 is one of the methods for powder compaction in the ceramic fabrication. The powder is pressed about 200 megapascal (MPa) and the method of the pressing is two times pressing. The holding time for the pressing is about 1000 ms.

Figure 2.3 Uniaxial Pressing Machine

Lastly, the sintering process took placed. Sintering process is a heat treatment process in order to form the microstructure of the ceramic body in which the powders are bonded to keep hold of the required shape in producing the desired shape. The sintering rate of the temperature will increased by 2^{0} C/minute and the samples were hold for 1 hour as shown in Figure 2.4 then the samples were cooled in the furnace.